# 1

# Introduction

*Ruoqing Xu[1], Jie Wang[2], Lilin Zhang[1], and Jingjie Ge[1]*

[1] The Hong Kong Polytechnic University, Department of Applied Biology and Chemical Technology, 11 YuK Choi Road, Hung Hom, Kowloon, HongKong
[2] Xihua University, Key Laboratory of Fluid and Power Machinery of Ministry of Education, Department of Materials Science and Engineering, School of Materials Science and Engineering, No. 9999, Hongguang Street, Pidu Area, Chengdu, 610039, China



With the current rapid growth of energy required by society, the rapid increase in fossil fuel consumption has led to a series of environmental pollution problems, such as global warming, ecosystem destruction, and air pollution. Therefore, the exploration of low-cost, green, and clean renewable energy conversion and storage technologies has become one of the most serious challenges facing today's society [1]. Electrochemical energy storage and conversion systems such as fuel cells [2], metal–air batteries [3], water electrolysis devices [4], and carbon dioxide capture, storage, and reduction technologies [5] have emerged as important ways of dealing with environmental and energy crises. Electrocatalysis is a key technology for energy conversion, as it accelerates electrochemical reactions essential for improving conversion efficiency. It plays a central role in reactions such as water splitting, carbon dioxide reduction reaction ($CO_2RR$), nitrogen reduction reaction ($N_2RR$), and the production of liquid fuels, etc. For example, in water splitting, electrocatalysis facilitates the decomposition of water into hydrogen, a clean energy source essential for establishing a low-carbon economy. Catalysts enhance the energy conversion efficiency of electrocatalysis by reducing the activation energy of the reactants and optimizing the reaction pathways and rates. However, one of the most critical challenges is identifying suitable catalysts for various electrocatalytic reactions. These materials are expected to demonstrate efficient electrocatalytic activity, selectivity, and stability to ensure long-term, reliable energy conversion performance. Consequently, the properties of the electrode materials, such as composition, surface structure, and morphology, have to be carefully controlled according to the electrochemical conditions to achieve efficient and high-performance electrocatalysis.

Functional materials offer more attractive solutions for sustainable energy conversion due to their lower costs and wider resource availability compared to conventional noble metal electrocatalytic materials [6, 7]. In addition, research on functional materials has facilitated the development of novel energy conversion

*Functional Materials for Electrocatalytic Energy Conversion*, First Edition.
Edited by Zhicheng Zhang, Meiting Zhao, and Yuchen Qin.

technologies. For instance, $CO_2RR$ enables the conversion of greenhouse gas $CO_2$ into valuable chemical fuels using renewable electricity, providing new opportunities to reduce resource extraction and achieve carbon neutrality [5, 8]. Similarly, $N_2RR$, which converts of $N_2$ to $NH_3$ by electrochemical reduction is considered a sustainable alternative process [9]. However, in electrocatalysis, the high dissociation energies of the C—O and N≡N bonds in the linear molecules of $CO_2$ and $N_2$ lead to their low chemical activity. The significant energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of $CO_2$ and $N_2$ molecules further enhances their chemical stability. Besides, the low proton affinity of $CO_2$ and $N_2$ complicates direct protonation [10–12]. These properties make $CO_2RR$ and $N_2RR$ challenging. Consequently, scientists are focusing on developing innovative electrocatalysts to overcome the challenges posed by the high dissociation energies and significant energy gaps of $CO_2$ and $N_2$, while enhancing their chemical reactivity and protons affinity. Functional materials based on covalent organic frameworks (COFs) have emerged as promising catalysts for the efficient utilization of $CO_2$. In particular, COF-based functional materials with multiple active sites, such as single-metal sites, metal nanoparticles, and metal oxides, offer great potential for realizing $CO_2$ conversion and energy storage [13]. Besides, the researchers also focused on the important effects of vacancies, high-index facets, lattice strain, lattice disorder, and polymer–inorganic interface configurations on the enhancement of $CO_2RR$ and $N_2RR$ performance. They noted that defect engineering can enhance $CO_2$ and $N_2$ uptake and tune the electronic structure of the catalyst. In terms of interfacial engineering, polymers play an important role as supports, modifiers, or blenders of polymer–inorganic composites. The introduction of polymers can inhibit hydrogen evolution reaction (HER), enhance the concentrations of $CO_2$ and $N_2$, stabilize intermediates, and change the electronic structure of the catalyst. This modulation affects the binding energies of $CO_2$, $N_2$, and intermediates on the catalyst surface, leading to more efficient reactions [14].

Despite the significance and promising prospects of the aforementioned electrocatalytic process, a common challenge in these reactions is the relatively low energy conversion efficiency, which remains far from industrial viability. Conventional electrocatalysts and energy storage materials still face technical problems, including complicated preparation processes, high cost, and inadequate catalytic activity and stability. These limitations severely restrict their commercialization and further applications. To enhance the reaction rates of promising catalytic reactions, there is a need for low-cost, highly active, and durable electrochemical materials. In recent years, functional materials, particularly metal- and carbon-based nanomaterials, have garnered significant attention from researchers due to their large specific surface area and high surface activity. Moreover, the bonding and electronic states on the surface of these nanocatalysts are different from those inside the particles, and the incomplete coordination of the surface atoms increases the number of surface-active sites, thereby improving catalytic performance. As a result, functional materials with specific morphologies and architectures show great promise for energy conversion applications. This book focuses on four different types of functional materials, including metal-based materials, metallic compounds,

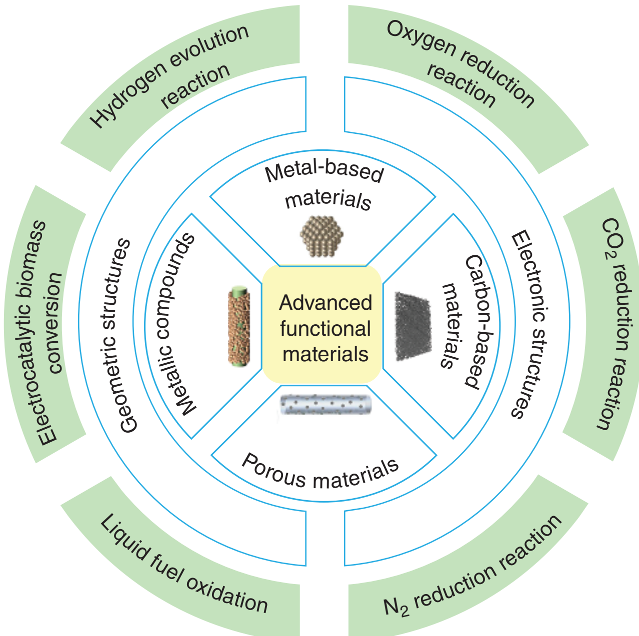


**Figure 1.1** Illustration of advanced functional materials for electrochemical catalysis.

carbon-based materials, and porous materials. By regulating their geometric structures and electronic structures, these functional materials demonstrate specific catalytic effects on various electrochemical reactions in practical applications. The facilitating role of functional materials as catalysts in electrocatalytic energy conversion is explored from several perspectives (Figure 1.1).

The catalytic performance of metal-based nanocatalysts is influenced by their geometric and electronic properties, including size, morphology, phase, atomic distance, and composition. For example, the density of active sites and lattice strain on the surface of nanoparticles can be modified by adjusting their shape and size, thereby enhancing catalytic activity and selectivity. The most commonly employed metal electrocatalysts are transition metals, such as platinum, palladium, copper, iron, and nickel. In addition to metal-based catalysts, metallic compounds also exhibit promising catalytic performances for various electrocatalytic processes. These compounds are typically formed from metallic and nonmetallic elements. Similarly, the performance of metal compound catalysts is influenced by their composition, structure, and surface properties. Common metallic catalysts include transition metal oxides, transition metal sulfides, and transition metal nitrides. The metal elements in these compounds often possess a variety of oxidation states and coordination environments, which enable them to interact effectively with reactants and modulate the rate and selectivity of catalytic reactions.

In addition to metal-based functional materials, carbon-based materials exhibit excellent properties for electrocatalytic applications. These materials feature a highly specific surface area and abundant pore structure, providing abundant reactive active sites and diffusion pathways to increase the reaction rate. Their good electrical conductivity and chemical stability enable efficient electron transfer during catalytic reactions, allowing them to tolerate harsh conditions such as high temperatures, acid, and alkali. Moreover, carbon-based nanocatalysts possess tunable surface chemistry, and their catalytic activity and selectivity can be adjusted by introducing or modifying surface functional groups, demonstrating excellent catalytic performance in several fields. On the other hand, porous materials as a fundamental category of functional materials also have garnered significant attention and undergone extensive research. Their highly porous structures provide large specific surface areas and pore volumes, facilitating the regulation of adsorption, diffusion, and reaction processes based on different pore sizes. The tunable pore structure and distribution expose various types of active sites on their surfaces, providing abundant opportunities for various catalytic applications. Currently, various types of porous material catalysts have been developed, including metal–organic framework materials (MOFs), mesoporous silica materials (e.g. SBA-15 and MCM-41), oxides (e.g. zirconia, alumina), and carbon-based materials (e.g. activated carbon and carbon nanotubes). Researchers are dedicated to designing and synthesizing novel porous materials to further optimize their catalytic properties and advance catalytic science and engineering.

This book provides a comprehensive overview of functional materials and their specific performances in electrocatalytic energy conversions. We focus on metallic compounds, metal-based materials, carbon-based materials, and porous materials. By studying and optimizing the electrocatalytic properties of these functional materials, we aim to advance the development of electrocatalytic energy conversion technologies and contribute to the revolution toward sustainable energy. The goal of this book is to deepen readers' understanding of functional materials for electrocatalytic energy conversion while offering insights for future research and applications. We hope that through continuous innovation and collaboration, we can overcome the challenges we currently face and pave a way for a more sustainable and cleaner energy future.

## Acknowledgment

The work was financially supported by the Hong Kong Polytechnic University (grant no. P0047728), the Key Project of Xihua University (grant no. Z222070), and Chengdu Vehicle Environmental Protection Technology Co., Ltd, (No. 2023-CDVEPTKF-04).

## References

1 Zhang, J.N. (ed.) (2022). *Carbon-based Nanomaterials for Energy Conversion and Storage: Applications in Electrochemical Catalysis*, Springer Series in Materials Science, vol. 325. Springer.

**2** Bailey, A., Andrews, L., Khot, A. et al. (2014). Hydrogen storage experiments for an undergraduate laboratory course—clean energy: hydrogen/fuel cells. *J. Chem. Educ.* 92 (4): 688–692.

**3** Wang, H.-F. and Xu, Q. (2019). Materials design for rechargeable metal-air batteries. *Matter* 1 (3): 565–595.

**4** Zhang, J., Zhang, Q., and Feng, X. (2019a). Support and interface effects in water-splitting electrocatalysts. *Adv. Mater.* 31 (31).

**5** de Jesus Gálvez-Vázquez, M., Moreno-García, P., Xu, H. et al. (2020). Environment matters: $CO_2$RR electrocatalyst performance testing in a gas-fed zero-gap electrolyzer. *ACS Catal.* 10 (21): 13096–13108.

**6** Kulkarni, A., Siahrostami, S., Patel, A., and Nørskov, J.K. (2018). Understanding catalytic activity trends in the oxygen reduction reaction. *Chem. Rev.* 118 (5): 2302–2312.

**7** Wang, G., Jia, S., Gao, H. et al. (2023). The action mechanisms and structures designs of F-containing functional materials for high performance oxygen electrocatalysis. *J. Energy Chem.* 76: 377–397.

**8** Xue, D., Xia, H., Yan, W. et al. (2020). Defect engineering on carbon-based catalysts for electrocatalytic $CO_2$ reduction. *Nanomicro Lett.* 13 (1): 5.

**9** Tong, W., Huang, B., Wang, P. et al. (2020). Crystal-phase-engineered PDCU electrocatalyst for enhanced ammonia synthesis. *Angew. Chem.* 132 (7): 2671–2675.

**10** Li, L., Li, X., Sun, Y., and Xie, Y. (2022). Rational design of electrocatalytic carbon dioxide reduction for a zero-carbon network. *Chem. Soc. Rev.* 51 (4): 1234–1252.

**11** Shen, H., Choi, C., Masa, J. et al. (2021). Electrochemical ammonia synthesis: mechanistic understanding and catalyst design. *Chem* 7 (7): 1708–1754.

**12** Pan, F. and Yang, Y. (2020). Designing $CO_2$ reduction electrode materials by morphology and interface engineering. *Energy Environ. Sci.* 13 (8): 2275–2309.

**13** Lu, M., Zhang, M., Liu, J. et al. (2022). Covalent organic framework based functional materials: important catalysts for efficient $CO_2$ utilization. *Angew. Chem.* 134 (15): e200200003.

**14** Chen, Y., Chen, C., Cao, X. et al. (2023). Recent advances in defect and interface engineering for electroreduction of $CO_2$ and $N_2$. *Acta Phys. -Chim. Sin.* 0 (0): 2210053.